Laser cladding with HA and functionally graded TiO$_2$-HA precursors on Ti–6Al–4V alloy for enhancing bioactivity and cyto-compatibility

Rasmi Ranjan Behera$^a$, Abshar Hasan$^b$, Mamilla Ravi Sankar$^{b,*}$, Lalit Mohan Pandey$^b$

$^a$ Department of Mechanical Engineering, Indian Institute of Technology Guwahati, Assam 781039, India
$^b$ Department of Biosciences and Bioengineering, Indian Institute of Technology Guwahati, Assam 781039, India

**Abstract**

In the present study, the morphology and composition of Titanium alloy (Ti–6Al–4V) surfaces were modified by laser cladding (LC) process to enhance the biocompatibility and bioactivity of orthopaedic implants. Ti–6Al–4V substrates were processed using a pulsed Nd:YAG laser with various precursors: 100% HA and functionally graded TiO$_2$-HA material (FGM). A set of laser parameters having 21.6 J/mm$^2$ laser energy density or irradiance was applied for cladding, to execute a comparative study. The morphology, phases and wettability with different biological tests including bioactivity, protein adsorption, cell adhesion and cyto-compatibility were performed on cladded samples. The FGM cladding showed higher apatite precipitation than 100% HA cladding. Both LC samples had significantly higher amount of protein adsorption lead to higher cell adhesion and cyto-compatibility compared to non-cladded Ti-6Al-4 V alloy. In between the LC samples, FGM cladding had more protein adsorption and cell adhesion than 100% HA cladding. With six days of incubation, the proliferation rate of FGM cladding showed higher apatite precipitation than 100% HA cladding. Both LC samples had significantly higher amount of protein adsorption lead to higher cell adhesion and cyto-compatibility compared to non-cladded Ti-6Al-4 V alloy. In between the LC samples, FGM cladding had more protein adsorption and cell adhesion than 100% HA cladding. With six days of incubation, the proliferation rate of FGM cladding (215.6 ± 17.2%) was significantly higher than 100%HA cladding (134.6 ± 9.5%) and non-cladded Ti–6Al–4 V control (100%). All these outcomes reveal that the LC process improves the biocompatibility and bioactivity of Ti–6Al–4 V.

**1. Introduction**

Demand for artificial implants for orthopaedic and dental applications has been increasing in recent days. Thus different studies have been carried out to develop and improve the quality of implant regarding its functionality, durability and biological response. Biomaterials, which are either modified naturally or chemically synthesized, have been successfully used in different implants for repair or replacement of natural tissues. Calcium phosphate (Ca-P) based hydroxyapatite (HA, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$), is the most widely used biomaterial which has similar mineral constituents found in teeth and bones [1]. HA has the potential to combine with host tissue and stimulate strong bonding at the interface of tissue and material. It can help to grow the tissues and ignore the unexpected outcomes from immune system [2,3]. However, HA alone cannot be used as a bulk material for load-bearing implants due to its lower fracture toughness and lower fatigue strength. Thus, HA coating on bio-inert metal such as Ti-6Al-4 V alloy was developed to achieve the superior mechanical performance of the metal as well as excellent bioactivity of HA simultaneously.

To modify the surface of a metal alloy by Ca–P based surface chemistry, several techniques have been applied to enhance bioactivity and biocompatibility of the implant. These techniques include electro-phoretic deposition [4], ion-beam sputtering [5], magnetron sputtering [6,7], plasma spraying [8], and sol-gel coating [9]. Also, pulsed laser deposition is used to irradiate Ca–P from the target material and deposit on metal alloy [10,11]. Surface coatings with the nanoscale thickness of silanes self-assembled monolayers (SAMs) have also been used to improve the biocompatibility of the materials with controlled wettability and surface chemistry [12,13]. However, most of the above mentioned methods neither provide strong adherence of the coating to substrate nor textured surface for attachment and growth of new bone cell at the tissue implant interface. Hence, laser cladding (LC) process was developed to fabricate Ca–P coatings due to its ability to form a strong metallurgical bonding between the coated material and Ti-6Al-4 V substrate. Also, LC has the potential to obtain suitable surface chemistry and surface textures to enhance the biocompatibility as well as bioactivity of metallic surfaces at tissue–implant interface [14].

LC is a thermo-chemical process where a non-treated surface being melted with the coating material by application of high power laser beam onto a small area. So, the initial properties of metal surface is modified which leads to inter-metallic bonding between coating and substrate with little dilution [15]. The deposited material can be